

METHOD OF FILM DEPOSITION, AND FABRICATION OF STRUCTURES

DESCRIPTION

5                   Field of the Invention

The present invention relates to a method of fabricating electronic devices that contain at least a layer of aluminum oxide deposited by chemical vapor deposition  
10           (CVD) or atomic layer deposition (ALD) utilizing aluminum alkoxide precursors and deposition temperatures greater than 500°C.

15                   Background of the Invention

In the quest for improved performance, electronic circuits are becoming denser and devices smaller. For example, the most common gate dielectric in metal oxide semiconductor field effect transistors (MOSFET) has been SiO<sub>2</sub>. However,  
20           as the thickness of SiO<sub>2</sub> approaches 20 Å, substantial problems appear, including large leakage currents through the gate dielectric, long term dielectric reliability, and difficulty of manufacture and thickness control. One solution to the above problems is to use thick films of  
25           materials such as aluminum oxide which have a dielectric constant larger than SiO<sub>2</sub>. Thus, the physical thickness of the gate dielectric can be large while the electrical equivalent thickness relative to SiO<sub>2</sub> films can be scaled. The electrical equivalent thickness,  $t_{eq}$ , of a high  
30           dielectric constant material, relative to SiO<sub>2</sub>, for example, may be calculated using the formula:

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$$t_{eq} = t_{phy} (\epsilon_{SiO_2} / \epsilon_{high \ K})$$

where  $t_{phy}$  is the actual thickness of the substitute metal oxide gate dielectric, such as aluminum oxide and  $\epsilon_{SiO_2}$  and  $\epsilon_{high \ K}$  are the dielectric constants of  $SiO_2$  and the metal oxide gate dielectric film, respectively.

Similar problems are encountered in scaling capacitors in memory devices. As the circuits become denser and the devices smaller, a material with a higher capacitance such as aluminum oxide is necessary to store adequate charge in the capacitor. Aluminum oxide has a dielectric constant of 10, which is more than double the dielectric constant of  $SiO_2$  ( $\epsilon=4$ ) and is thus an attractive material for replacement of  $SiO_2$  in transistors and capacitors.

However, CVD of aluminum oxide from alkyl aluminum CVD precursors, such as trimethylaluminum seems to be inherently contaminated with carbon; see R.S. Ehle, et al., J. Electron. Mater. Vol. 12, 1983, p.587. Similar carbon contamination is observed in aluminum oxide deposited from alkylaluminum alkoxides. XPS survey spectrum and Auger depth profile of aluminum oxide deposited at 400°C on Si with an alkylaluminum alkoxide (triethyldialuminum tri-sec-butoxide) show carbon contamination throughout the film. See, for example, T.M. Klein, et al., Appl. Phys. Lett., Vol. 75 1999, p.4001. Similar carbon contamination would be expected in films grown with similar alkylaluminum alkoxides as described, for example, in U.S. Patent No. 6,037,033. Aluminum oxide has been deposited using aluminum  $\beta$ -diketonates, such as aluminum tris(2,4-pentanedionato) and aluminum tris(tetramethylheptanedionato). However  $\beta$ -diketonates are known to undergo complex decomposition

pathways which may lead to carbon incorporation in the film. Low deposition temperatures and addition of H<sub>2</sub>O as an oxidant are recommended to obtain aluminum oxide films; See, J.S. Kim, et al., Appl. Phys Lett., 62(7) 1993 P.681.

5 However, low deposition temperatures and water results in a porous film with excess OH. Deposition of aluminum oxide from AlCl<sub>3</sub> and H<sub>2</sub> and CO<sub>2</sub> has been described in U.S. Patent No. 4,097,314. An incubation period of about 30 seconds is necessary before film growth occurs which results in an  
10 uncertainty in controlling growth rates of thin films (less than 1000 Å). Residual Cl and H contaminates are present in the film. Additionally AlCl<sub>3</sub> is highly corrosive generating HCl as a byproduct.

15 Deposition of aluminum oxide from aluminum alkoxides is known and deposition of aluminum oxide at temperatures less than 500°C has been described; See, for example, J.A. Aboaf, J. Electrochem. Soc. 1967, Vol. 114(9), p.948; J. Fournier, Mat. Res. Bull., 23 31 (1988); and H. Mutoh, J.  
20 Electrochem. Soc. 122, 987 (1975). Deposition of aluminum oxide with aluminum isopropoxide deposited on Si at 740°C has been reported by S.S. Yom et al., Thin Solid Films, 213, 72, 1992. However, as described in U.S. Patent Nos. 5,431,734, 5,540,777, 5,648,113, and 5,728,222, aluminum  
25 alkoxides are known to isomerize during heating and delivery resulting in unreproducible precursor delivery and film growth. Moreover the aforementioned U.S. patents describe methods and apparatuses for depositing aluminum oxide from aluminum isopropoxide utilizing FTIR monitoring  
30 of the aluminum isopropoxide vapor from a bubbler to improve reproducibility. Despite the improved reproducibility, the '734, '777, '113 and '222 patents

suffer from the disadvantage of using conventional bubbler technology.

5 The other previous work with aluminum alkoxides patents  
also have utilized conventional bubbler technology which  
involves a carrier gas bubbled through a neat (i.e.,  
without solvent) precursor at an elevated temperature. The  
conventional bubbler technology relies on a consistent  
10 vapor pressure of the precursor to deliver a uniform  
precursor flux to the film. In addition, because vapor  
pressure is directly related to temperature, conventional  
bubbler technology suffers from the disadvantages of  
needing to maintain a bubbler temperature with minimal  
variation during a run and from run to run. Fluctuations  
15 in precursor flux are known to result in variable film  
growth rates. Solid compounds are known to sinter and  
change surface area over time, resulting in nonuniformity  
in film growth rates from run to run. Sintering is not a  
problem for liquid precursors, but over time the liquid  
20 precursors may degrade from the thermal cycling and thermal  
load placed on the precursor. Additionally, at elevated  
temperatures, decomposition processes are accelerated. As  
described in U.S. Patent Nos. 5,431,734, 5,540,777,  
5,648,113, and 5,728,222, elevated temperatures and thermal  
25 cycling of aluminum alkoxide during vaporization in a  
conventional bubbler contributes to premature degradation  
of the aluminum alkoxide over time. Aluminum alkoxides  
change their chemical state by ligand rearrangement,  
cluster formation, or oxidation. Aluminum alkoxides are  
30 known to react with water or oxygen inadvertently  
introduced into the bubbler through inadequately purified  
carrier gases bubbled through the precursor, air leaks, or

water and oxygen adsorbed on the bubbler walls. Furthermore, aluminum alkoxides are known to isomerize during heating resulting in many different species with varying vapor pressures, with the result that consistent  
5 vapor pressure is difficult to achieve with conventional bubbler technology.

An additional difficulty of depositing aluminum oxide by CVD is that aluminum oxide exists in a number of  
10 morphological forms. The aluminum oxide polymorph obtained is critically dependent on deposition conditions, such as the CVD precursor, oxidant, growth temperature and pressure, and substrate. Additionally, the only thermally  
15 stable modification of aluminum oxide is  $\alpha$ -alumina ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, corundum or sapphire). All other polymorphs are metastable and irreversibly converted to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at sufficiently high temperatures.

An additional difficulty of fabricating devices on silicon  
20 with aluminum oxide deposited on Si by CVD is the potential growth of an interfacial oxide layer during deposition or during post deposition processing. See for example, T.M. Klein, et al., Appl Phys. Lett., Vol 75 1999, p. 4001.

25 In view of the drawbacks with prior art processes of forming aluminum oxide films, there is a continued need for developing a new and improved method for depositing aluminum oxides which avoids each of the above mentioned  
30 prior art problems.

### Summary of the Invention

The present invention relates to a method of depositing aluminum oxide films by chemical vapor deposition (CVD) or atomic layer deposition (ALD). The present invention is also directed to a method of fabricating electronic devices that contain aluminum oxide deposited by the inventive method. Suitable electronic devices that can be fabricated in the present invention include, but are not limited to: transistors, capacitors, diodes, resistors, switches, light emitting diodes, lasers, wiring structures, interconnect structures or any other structure wherein the aluminum oxide film of the present invention can be incorporated therein.

In a broad aspect, the present invention relates to chemical vapor deposition or atomic layer deposition of aluminum oxide utilizing an aluminum alkoxide precursor dissolved, emulsified or suspended in a liquid; vaporizing the aluminum alkoxide precursor; and depositing a constituent of the vaporized precursor on a substrate to form a film at a deposition temperature of greater than 500°C. In this aspect, the liquid may or may not be co-vaporized with the precursor. In one embodiment, the inert liquid is vaporized with the precursor. In an alternative embodiment, the inert liquid is not vaporized and is diverted from the reactor in liquid form. In yet another embodiment of the present invention, the deposited film is annealed after conducting the inventive processing steps.

Preferred aluminum alkoxide precursors that may be employed in the present invention include, but are not

limited to: aluminum iso-propoxide, aluminum  
sec-butoxide, aluminum ethoxide, aluminum iso-butoxide,  
aluminum methoxide, aluminum neo-pentoxide, aluminum  
propoxide, aluminum butoxide, aluminum tertiary-butoxide,  
5 or aluminum phenoxide.

Another aspect of the present invention relates broadly  
to the fabrication of multilayer structures incorporating  
aluminum oxide deposited by the inventive method.

10 Further aspects of the present invention include:

-Fabricating an electronic structure incorporating a film  
deposited by the inventive method.

15 -Fabricating a complementary metal oxide semiconductor  
(CMOS) integrated circuit (IC) logic device which  
contains both n-type field effect transistors (NFETs) and  
p-type field effect transistors (PFETs) formed on a  
20 single substrate incorporating a film deposited by the  
inventive method, as shown in FIG 1.

-Fabricating an integrated circuit capacitor  
incorporating a film deposited by the inventive method,  
25 as shown in FIG 2.

-Fabricating an integrated circuit wiring structure  
incorporating a film deposited by the inventive method,  
30 as shown in FIG 3.

### Brief Description of the Drawings

FIG 1 is an illustration of a cross-sectional view of a  
integrated circuit with both PFET and NFET devices on a  
single substrate.

FIG 2 is an illustration of a cross-sectional view of an  
integrated circuit capacitor.

FIGS 3A-B are illustrations of a cross-sectional view of  
an integrated circuit wiring structure.

FIG 4 is a FTIR spectrum of as deposited aluminum oxide  
films at various deposition temperatures.

FIG 5 is a FTIR spectrum of as deposited or as  
deposited/annealed aluminum oxide films.

FIG 6 is plot of capacitance, C, (pF) vs. voltage (V)  
showing high frequency (100 KHz) CV curves of Al oxide  
films with different thickness deposited at 500°C.

FIG 7 is a plot of capacitance, C, (pF) vs. Voltage, V,  
for Al oxide films deposited at 600°C and annealed in O<sub>2</sub>  
and forming gas.

FIG 8 is a plot showing the IV characteristics of films  
deposited at 500° and 600°C.

FIG 9 is a plot of  $t_{\text{qm}}$  (nm) vs.  $t_{\text{ph}}$  (nm) showing the  
dielectric constants of Al oxide films deposited at 500°C  
and annealed in O<sub>2</sub> and forming gas.



FIG 10 is a plot of the leakage current for various deposited and annealed aluminum oxide films.

FIG 11 is a schematic representation of a delivery system for chemical vapor deposition or atomic layer deposition of a film or coating.

FIGS 12A-H are illustrations of a cross-sectional view of a transistor containing a multilayer dielectric through various processing steps.

FIGS 13-22 are illustrations of a cross-sectional view of the fabrication of a transistor.

FIGS 23-27 are illustrations of a cross-sectional view of the fabrication of a stack capacitor.

FIG 28 is an illustration of a cross-sectional view of a trench capacitor.

#### Detailed Description of the Invention

As stated above, the present invention broadly relates to CVD or ALD of aluminum oxide, and fabrication of an electronic devices incorporating a film deposited by the inventive method. More specifically, the present invention relates to CVD or ALD of aluminum oxide utilizing an aluminum alkoxide precursor dissolved, emulsified or suspended in a liquid, vaporizing the aluminum alkoxide precursor so as to form a vaporized precursor, and depositing a constituent of the vaporized precursor on a substrate to form a film at a deposition

temperature of greater than 500°C. More particularly, the deposition is carried out at a temperature of from about 500° to about 1200°C. Following the deposition of the aluminum oxide film, the film may be annealed utilizing any conventional annealing process such as a forming gas anneal.

The precursor is defined in the present invention as any aluminum alkoxide. A generalized formula for the precursor of the present invention is  $\text{Al(OR)}_3$ , where R is a ligand selected from linear or branched  $\text{C}_1\text{-C}_{12}$  alkyls. The preferred precursors are aluminum iso-propoxide, aluminum sec-butoxide, aluminum ethoxide, aluminum isobutoxide, aluminum methoxide, aluminum propoxide, aluminum butoxide, aluminum tertiary-butoxide, or aluminum phenoxide.

The liquid is selected from aliphatic hydrocarbons, aromatic hydrocarbons, alcohols, ethers, aldehydes, ketones, acids, phenols, esters, amines, alkyl nitriles, halogenated hydrocarbons, silylated hydrocarbons, thioethers, amines, cyanates, isocyanates, thiocyanates, silicone oils, nitroalkyls, alkyl nitrates and/or mixtures of one or more of the above. The precursor may be dissolved, emulsified or suspended in the liquid using techniques well known to those skilled in the art.

Vaporization is carried out by heating the precursor and liquid to a temperature of from about 40° to about 250°C for a time period sufficient to convert the liquid precursor into a vaporized precursor. The vaporization may be carried out in the presence of an inert gas such

as He, N<sub>2</sub> or Ar, which gas may also be used during the deposition of the aluminum oxide.

5 The method of aluminum oxide deposition of the present invention can be used in any CVD or ALD process with any delivery means using any number of co-reactants. Thus, the invention is not limited to a specific CVD or ALD apparatus or delivery system. Chemical vapor deposition (CVD) is defined as introduction of multiple reagents  
10 into a reactor simultaneously. Atomic layer deposition (ALD) is defined as sequential introduction of multiple reagents into a reactor, including, but not limited to: atomic layer epitaxy, digital chemical vapor deposition, pulsed chemical vapor deposition and other like methods.

15 One aspect of the present invention relates broadly to fabrication of a structure of a complimentary metal oxide semiconductor (CMOS) integrated circuit logic device  
20 incorporating aluminum oxide deposited by the inventive method. More specifically, the present invention relates to the fabrication of a CMOS integrated circuit containing both n-type field effect transistors (NFETs) and p-type field effect transistors (PFETs) formed on a  
25 single substrate. As shown in FIG 1, NFET device 11 is formed on a p-type conductivity region 13 of substrate 10 and contains a gate electrode 14 formed on a gate dielectric 15 and a pair of n-type source/drain regions 16 formed on laterally opposite sides of gate electrode  
30 14 is noted that the ohmic contacts are not shown in FIG 1.

Similarly, PFET device 17 is formed on a n-type conductivity region 18 of substrate 10 and contains the gate electrode 19 formed on gate dielectric 15 and a pair of p-type conductivity source/drain regions 20 formed along opposite sidewalls of gate electrode 19. The ohmic contacts are not shown. The NFET and PFET devices are separated by shallow trench isolation 21 and by spacers 22. In this aspect of the invention, gate dielectric 15 incorporates aluminum oxide deposited by the inventive method.

Another aspect of the present invention relates broadly to fabrication of a structure of an integrated circuit capacitor incorporating aluminum oxide deposited by the inventive method. More specifically, the present invention relates to the fabrication of a capacitor. As shown in FIG 2, a typical capacitor is formed on a substrate 30, connected by a plug 31 to a transistor, with a barrier 32 and consists of a bottom electrode 33, a dielectric material 34 which may or may not be ferroelectric, and a top electrode 35. In this aspect of the present invention, the dielectric material 34 incorporates aluminum oxide deposited by the inventive method. The capacitor may be stack or trench.

A yet further aspect of the present invention relates broadly to fabrication of a structure of an integrated circuit wiring structure incorporating aluminum oxide deposited by the inventive method. As shown in FIG 3A, a typical wiring structure is formed by etching trenches 41 and vias 42 into a dielectric layer 43. Below dielectric layer 43 is a metal thin film wire 44 and a dielectric

layer 45 of a wiring layer. In FIG 3B, the trench and via are filled with a barrier material 46 and a wiring metal 47. In this aspect of the invention, the dielectric material 43 or 45 incorporates aluminum oxide deposited by the inventive method.

5

The above is a generic description of the present invention, the following description provides specific details of the present invention. It should be noted that in each of the above described electronic devices conventional techniques are used in conjunction with the presently described method.

10

# EXAMPLE 1

## Chemical Vapor Deposition of Aluminum Oxide

5 The aluminum oxide films were deposited in a quartz  
horizontal hot wall CVD reactor equipped with a 1x3x8"  
quartz flow cell. An ATMI (Advanced Technology and  
Materials, Inc. Danbury, CT) LDS 300B liquid delivery  
10 system and vaporizer was used to introduce precursors  
into the reactor. The aluminum alkoxide source mixture  
was comprised of 40 grams of aluminum iso-propoxide,  
 $\text{Al}(\text{i-OC}_3\text{H}_7)_3$ , and 1 liter of iso-propanol. A thin layer  
(less than 20 Å) of  $\text{SiO}_x\text{N}_y$  was deposited on a silicon  
15 wafer prior to growth of aluminum oxide. The aluminum  
alkoxide source mixture was flowed at 0.2-0.05 ml/min,  
preferably 0.05 ml/min. The vaporizer temperature was  
120-180°C, preferably 120°C. Anhydrous nitrogen was  
introduced into the vaporizer at 20-2000 sccm, preferably  
200 sccm as a carrier gas for the volatilized aluminum  
20 iso-propoxide. A mixture of nitrogen and oxygen was  
introduced through a separate inlet as the reactant gas.  
The system pressure was 5 Torr during growth. The  
substrate was heated by an external high intensity  
infrared lamp and the susceptor was comprised of  
25 Hastalloy. The temperature of the susceptor was  
monitored by insertion of a thermocouple into the  
susceptor. Aluminum oxide was deposited at 350-700°C,  
preferably at temperatures of greater than 500°C.

30 As shown in the FTIR spectra of the as deposited films  
(see FIG 4), the aluminum oxide films deposited at 350°C  
and 400°C contained a broad absorption band at 3700-3000

cm<sup>-1</sup> which is assigned to O-H stretching vibrations of OH and H<sub>2</sub>O in the as deposited aluminum oxide films.

However, at deposition temperature of 500°C and greater, no absorption band at 3700-3000 cm<sup>-1</sup> was observed.

5 A distinctive narrow sharp strong absorption was observed at 581 cm<sup>-1</sup> in the spectra of aluminum oxide deposited at 350°C, 400°C, and 500°C. Aluminum oxide with similar absorption spectra have been defined as γ-Al<sub>2</sub>O<sub>3</sub>. At a deposition temperature of 600°C and 700°C, the peak at 581  
10 cm<sup>-1</sup> was not observed and the strong absorption band 1000 and 400 cm<sup>-1</sup> narrowed, signifying a different polymorph of aluminum oxide. No peaks assignable to SiO<sub>2</sub> were observed in the FTIR spectra of the as deposited films.

15 The as deposited films were annealed at 1000°C for 30 min in oxygen. As shown in the FTIR spectra of the annealed films (FIG 5), the aluminum oxide films deposited at 400°C had strong absorptions assignable to SiO<sub>2</sub>. The strong absorptions at 1200 and 1080 cm<sup>-1</sup> are ascribed to  
20 the LO and TO components of the asymmetric stretch of the SiO<sub>4</sub> unit, respectively. The absorption bands at 800 cm<sup>-1</sup> and 450 cm<sup>-1</sup> are attributed to skeletal network Si-O-Si symmetric stretching and bond bending, respectively. The remaining absorption bands are assigned to Al-O  
25 stretching and bending vibrations. However, in the spectra of the aluminum oxide film deposited at 600°C, the relative peak intensities and areas of the absorptions assigned to SiO<sub>2</sub> (1200, 1080, 800 and 450  
30 cm<sup>-1</sup>) was reduced relative to the absorptions assigned to Al-O. It is believed that the aluminum oxide deposited at temperatures less than 500°C which contain significant quantities of OH and/or absorbed water as observed in the

FTIR spectra are less dense, contain an excess of oxygen and more readily allow the diffusion of oxygen through the film facilitating the formation of an interfacial oxide layer during post deposition annealing.

5

Aluminum oxide films were analyzed for carbon content by nuclear reaction analysis (NRA). The samples were analyzed for total C and O using a 1.05 MeV beam of deuterons and the  $^{16}\text{O}(\text{d,p})^{17}\text{O}^*$  and  $^{12}\text{C}(\text{d,p})^{13}\text{C}$  nuclear reactions. Each sample was run three times to check its stability during irradiation. Due to the low stopping power of the particles and the large positive Q-values, these reactions have poor depth sensitivity, and cannot be used to directly separate contributions from the surface or substrate. First, a linear background was subtracted from the  $^{16}\text{O}(\text{d,p})^{17}\text{O}^*$  reaction peak in all spectra. A 1000 Å  $\text{SiO}_2$  standard was used to normalize the oxygen data. Since the reaction yield is constant to within  $\pm 5\%$  over this depth range, the average value was used to reduce the analysis to simple ratios of the reaction yields. A density of 2.3 was assumed, to give an areal density for this standard of  $4.6\text{E}17$   $^{16}\text{O}/\text{cm}^2$ . Next, a linear background was subtracted from the  $^{12}\text{C}(\text{d,p})^{13}\text{C}$  reaction peak in all spectra. A 20 microgram/ $\text{cm}^2$  carbon foil on a Si substrate was used to normalize the carbon data. The reaction yield is constant to within  $\pm 3\%$  over this depth range, so as in the case of the oxygen analysis, an average value was used to simplify the analysis. The areal density used for this sample was  $1.0\text{E}18$   $^{12}\text{C}/\text{cm}^2$ . Finally, these numbers for carbon are very close to the surface contamination levels one normally sees on an uncleaned



sample. To get an estimate of this, three more runs were conducted under the same conditions on plain silicon wafers having nothing but native oxide. Under ion beam bombardment, the carbon reaction yield first decreases slightly, (due to desorption of volatile organics) and then increases slowly and steadily (due to cracking of residual hydrocarbons in the vacuum system at the point of beam incidence). Two runs on virgin spots gave results of  $12.8 \pm 0.5$  and  $17.7 \pm 0.6$  in the above units. A third run on a spot that had 20x the normal exposure to the beam gave a result of  $40 \pm 1$ . From this, the surface carbon added during the run was no more than  $2E14 \text{ }^{12}\text{C}/\text{cm}^2$ , and that an average surface contribution of  $15E14 \text{ }^{12}\text{C}/\text{cm}^2$  could be subtracted from the above carbon results.

As summarized in Table 1, minimal carbon was observed by nuclear reaction analysis. As deposited aluminum oxide films grown at  $600^\circ\text{C}$  contained 0.06 atomic percent of carbon, whereas films grown at  $400^\circ\text{C}$  or less contained about 1% atomic percent of carbon. Annealing the as deposited films in oxygen at  $600^\circ\text{C}$  for 30 minutes did not affect the carbon levels in the film within experimental variation.

Table 1. Carbon content of aluminum oxide films as determined by nuclear reaction analysis.

T <sub>deposition</sub>	thickness	As Reacted	Annealed
°C	nm	atomic% C	atomic% C
350	1,626	1.4	1.5
0	732	1	0.8
375	343	1	0.9
400	979	1.2	1.4
400	400	1	1.1
500	1,019	0.2	0.2
600	1,280	0.06	0.03

The Al oxide films deposited on Si wafers were characterized electrically by capacitance-voltage (CV), See FIGS 6 and 7, and current-voltage (IV) measurements, See FIG 8. Capacitor fabrication suitable for electrical testing is described below.

After Al oxide deposition as described above, capacitors were formed by Al evaporation through a metal mask with the substrates held at room temperature. Prior to depositing the Al contacts the films were annealed in O<sub>2</sub> at 600°C for 30 min and forming gas (FG) at 550°C for 30 min. The area for these metal contacts was  $5.4 \times 10^{-4} \text{ cm}^2$ . The capacitors were fabricated on n-type Si substrates with P doping at about  $1 \times 10^{15} \text{ cm}^{-3}$ .

Specifically, FIG 6 shows a family of high frequency (100 KHz) CV curves of Al oxide films with different thickness deposited at 500°C. A detailed description of the CV characteristics of MOS capacitors can be found in S. M. Sze, "Physics of Semiconductor Devices", Chapter 7, second edition, Wiley Interscience, 1981. It is noted that for voltages above 1 V the capacitance saturates at some fixed value. This is defined as accumulation capacitance which is given by  $C_o = (K_o KA) / t_{ph}$  where  $K_o$  is the permittivity in vacuum,  $K$  is the dielectric constant of the insulator,  $A$  is the capacitor area and  $t_{ph}$  is the insulator physical thickness. Thus, the higher the accumulation capacitance for a given capacitor area,  $A$ , the thinner is the oxide film as shown in FIG 6. If  $K$  is normalized to the  $SiO_2$  dielectric constant of 3.9, then the physical thickness is expressed as an equivalent thickness. In order to increase circuit performance, low  $t_{eq}$  are desirable. Furthermore, when the oxide is very thin, very high electric fields are generated at the interface with the result that the classical formula is not correct and should be corrected for quantum effects. Simulations by Lo, et al., IEEE Elect. Dev. Lett. 18, 209 (1997), relate the accumulation capacitance to the a quantum mechanical physical thickness  $t_{qm}$ . In the present analysis,  $t_{qm}$  rather than  $t_{eq}$  is used.

Another important feature of the CV characteristics is "flatband". Flatband voltage is defined as the voltage where the semiconductors energy bands are flat with respect to the applied voltage. For an ideal condition this occurs at  $V=0$ . In general, non ideal flat band shifts are observed in metal oxide semiconductor (MOS) capacitors because of

non ideal conditions. Excessive charge in the films or at the oxide/Si interface can produce non ideal shifts. Also, different metals deposited on the oxide produce flat band shifts because of their inherent different work function values.

In general, for the low doping substrates used here flat band occurs for capacitance values below 100 pF. Flat band shift measured on the capacitor with low  $t_{qm}$  (high accumulation capacitance) is about -0.6/0.7V. By subtracting -0.3 V correction for Al work function flat band condition occurs at a voltage of about -0.3/0.4 V instead of V=0. Thus, some charge at the interface or in the bulk  $Al_2O_3$  may exist. Note also that some hysteresis is present in the CV characteristics, indicating undesirable film charge trapping.

Dielectric constant values of the Al oxide were measured by using a linear fit of the oxide quantum mechanical thickness extracted from CV characteristics versus the physical oxide thickness determined by n&k analysis (n&k Analyzer, n&k Technology, S. Clara , California). By assuming that the total capacitance is represented by an interfacial  $SiO_2$  capacitance in series with a high K dielectric film capacitance and using the parallel plate capacitor equation, the equivalent quantum mechanical  $t_{qm}$  (or classical  $t_{eq}$ ) thickness versus the physical thickness  $t_{ph}$  can be written as:

$$t_{qm}(t_{eq}) = t_{ox} + t_{ph}(K_{ox}/K)$$

where  $t_{ox}$  is the interfacial oxide thickness and  $K_{ox}$  is the interfacial oxide dielectric constant. In this analysis,  $K_{ox} = 3.9$  ( $SiO_2$  dielectric constant). The quantum mechanical thickness  $t_{qm}$  was calculated according to an IBM simulator, based on the "Lo et al." reference, requiring the dot area and accumulation capacitance value at about 2.1 V. From the measured electrical and physical thickness values, the dielectric constant  $K_{qm}$  and the residual interfacial layer  $R_{qm}$  thickness were then extracted via equation (3), using a least square fitting procedure.

The results for the Al oxide films deposited at 500°C and annealed in  $O_2$  and FG are shown in FIG 9. Dielectric constant is about 10 and the residual  $SiO_2$  layer about 1.3 nm.

FIG 7 shows a family of CV curves for Al oxide films deposited at 600°C and annealed in  $O_2$  and FG as above. The curve with low  $t_{qm}$  (high accumulation capacitance) shows a flatband shift of about -0.65 V which is about -0.35V from ideal when corrected for the Al work function. Note that the hysteresis for the low  $t_{qm}$  (~1.8) film is very small <10mV. FIG 7 indicates that the residual interfacial layer may also be reduced to a few Angstroms when compared with the 500°C process. In general, the 600°C process produced better electrical performance than 500°C because of the reduced hysteresis and reduced interfacial layer thickness.

Main motivation behind the use of high-K dielectric material for  $SiO_2$  gate replacement is the use of thicker dielectrics which can reach oxide equivalent thickness of

10 Å or below maintaining lower leakage currents than SiO<sub>2</sub>. FIG 8 shows IV characteristics of films deposited at 500°C and 600°C. The current densities at 1 V are plotted again in FIG 10. As can be seen, for Al oxide films deposited at 600°C leakage reduction is about 3 orders of magnitude when compared with the equivalent SiO<sub>2</sub> oxide thickness. Again the 600°C deposition process show lower leakage than the 500°C process where leakage reduction was only 15 times with respect to SiO<sub>2</sub> .

Based on the above disclosed results, it is desirable in the present invention to set the growth temperature of aluminum oxide to temperatures greater than 500°C.

## EXAMPLE 2

### Chemical Vapor Deposition of Aluminum Oxide

5 In this embodiment, the liquid is not vaporized and is diverted from the CVD or ALD reactor. The aluminum alkoxide is dissolved, emulsified or suspended in a liquid which vaporizes at a higher temperature. The aluminum alkoxide and the liquid is introduced into a vaporizer where the aluminum alkoxide is vaporized. The liquid is not vaporized, but instead is diverted from the reactor in liquid form.

15 One possible apparatus configuration is shown in FIG 11. As shown in this figure, the aluminum alkoxide and liquid (102) would flow from ampoule 100 to vaporizer 105 through outlet 104. The aluminum alkoxide is volatilized in the vaporizer, but the liquid is not. The vaporized aluminum alkoxide is then transported to reactor 110, and the nonvaporized inert liquid is drained out of the vaporizer and collected in trap 115. The vaporizer temperature is set at less than the boiling point of the liquid.

25 One preferred method would be aluminum isopropoxide and dodecane (boiling point 216°C) with the vaporizer temperature set at 120°C, and the deposition temperature greater than 500°C.

### EXAMPLE 3

#### Atomic Layer Deposition of Aluminum Oxide

- 5 In this embodiment, a substrate is placed in a suitable reactor for atomic layer deposition, for example the commercial F-200 reactor made by Microchemistry, and an aluminum oxide film is deposited. Atomic layer deposition is performed in a cyclic fashion with
- 10 sequential alternating pulses of vaporized aluminum alkoxide, reactant and purge gas (and/or vacuum evacuation of reactor chamber before introduction of aluminum alkoxide or reactant).
- 15 The aluminum alkoxide source mixture was comprised of 10 grams of aluminum iso-propoxide  $\text{Al}(\text{i-OC}_3\text{H}_7)_3$  and 1 liter of octane. In this example, the aluminum alkoxide source is vaporized in a vaporizer and the vapor is introduced into the reactor in a cyclical fashion. In order to
- 20 deposit aluminum oxide, an oxidant is introduced including, but not limited to: oxygen, ozone, water, hydrogen peroxide, nitrous oxide and combinations<sup>o</sup> thereof. The preferred oxidant is water.
- 25 The vaporizer temperature was 120°-180°C, preferably 120°C. Aluminum oxide was deposited at temperatures greater than 500°C. The aluminum alkoxide, reactant and inert purge gas ( $\text{N}_2$  or Ar or other inert gas) are pulsed into the reactor in the following sequence :
- 30
1. vapor of Al-containing aluminum alkoxide source mixture
  2. inert purge



3. reactant
4. inert purge

5 The aluminum alkoxide and reactant pulses (steps 1, and  
3) last 0.1 -1 second, preferably 0.5 seconds. The inert  
gas purge pulse (steps 2, and 4) last 0.2-5 seconds,  
preferably 2 seconds. Completion of steps 1 - 4 is a  
cycle, the completion of 1 cycle results in deposition of  
10 about 0.4-2 monolayer of aluminum oxide or roughly 0.1  
nm. In this example, the preferred thickness of  
deposited aluminum oxide containing film is 50 nm, so 500  
cycles of gas switching as described above are performed.

EXAMPLE 4  
Fabrication of a Transistor

5 In this embodiment, the inventive method is used to  
deposit aluminum oxide as gate dielectric layer 15 of the  
PFET and NFET as shown in FIG 1. A Si wafer substrate  
containing patterned structures is used. Selected  
10 regions of the substrate contain shallow trench isolation  
(STI) oxide located between the sites of transistor,  
other regions contain the field oxide, and selected  
regions of bare Si are exposed in the regions where  
transistor are to be located. The substrate is then  
placed in a suitable modular cluster tool, the surface of  
15 the bare Si is treated to form a  $\text{SiO}_x\text{N}_y$  layer in-situ  
without breaking vacuum, before a layer of aluminum oxide  
is deposited to a thickness of 1-100 nm using the CVD  
process of this invention. The wafer is then transported  
to a second module of the modular cluster tool where the  
20 gate electrode can be deposited on the aluminum oxide in  
situ without breaking vacuum.

For the deposition of the aluminum oxide using the  
inventive method, the aluminum alkoxide source mixture  
25 was composed of 40 grams of aluminum iso-propoxide in a  
liter of isopropanol. The aluminum alkoxide mixture was  
transported to a vaporizer where the mixture was  
vaporized at 120°C and the vapor transported into the  
chemical vapor deposition module of the cluster tool  
30 where an oxidant including, but not limited to: oxygen,  
ozone,  $\text{N}_2\text{O}$ , water, or mixtures thereof was present and an  
aluminum oxide film was deposited at 600°C.

#### EXAMPLE 5

Fabrication of a transistor utilizing aluminum oxide deposited by the inventive method as a component of a multilayer gate dielectric

In this embodiment, the inventive method is used to deposit a multilayer gate dielectric, 53 (See FIG 12H) where at least one of the layers is aluminum oxide doped or undoped. As shown in FIG 12H, a transistor device is formed on a conductivity region 54 and contains a gate electrode 52 formed on a gate dielectric 53 and a pair of n-type source/drain regions 51 formed on laterally opposite sides of gate electrode 52. The multilayer gate dielectric 53 is comprised of an optional upper layer, 57 which may act as a dopant diffusion barrier and stabilize the structure during deposition of the gate electrode 52. An optional lower layer 55 which may act as an electron barrier layer and as a layer to prevent oxidation of the underlying silicon during processing or both. The middle layer, 56, is a high-K dielectric layer. A suitable lower layer 55 is composed of dielectric materials including, but not limited to:  $\text{SiO}_2$ ,  $\text{SiO}_x\text{N}_y$ , or  $\text{Si}_3\text{N}_4$ , prepared from oxidation or nitridation of the silicon substrate or deposited separately. Other suitable lower layer materials include metal oxides or metal silicates. The high-K dielectric layer 56 is selected from the group consisting of aluminum oxide or a multilayer structure where at least one of the layers is aluminum oxide. The dielectric materials comprising the multilayer structure with aluminum oxide are selected from the group including, but not limited to:  $\text{Ta}_2\text{O}_5$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{HfO}_2$ ,

BaO, SrO, CaO, La<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, yttrium aluminate, lanthanum aluminate, lanthanum silicate, yttrium silicate, hafnium silicate, zirconium silicate, doped or undoped mixtures, layers or combinations thereof. The multilayer structure with aluminum oxide may be comprised of several layers of different materials such as a layer of hafnium oxide sandwiched between layers of aluminum oxide. The optional upper layer 57 may be an oxidized or nitrided surface of the middle layer, 56, or a deposited dielectric material including, but not limited to: SiO<sub>2</sub>, SiO<sub>x</sub>N<sub>y</sub>, Si<sub>3</sub>N<sub>4</sub>, ZrO<sub>2</sub>, HfO<sub>2</sub>, aluminum oxide, aluminosilicate, yttrium silicate, zirconium silicate, hafnium silicate, lanthanum silicate doped or undoped mixtures, layers or combinations thereof. Preferred gate dielectrics are comprised of a lower layer of SiO<sub>x</sub>N<sub>y</sub>, a layer of aluminum oxide, and an upper barrier layer of nitrided aluminum oxide. The aluminum oxide in the gate dielectric 53 is deposited by the inventive method.

FIGS 12A-12H are cross sectional views showing one preferred means for fabrication of a transistor shown in FIG 12H using the inventive method. Fabrication of the gate dielectric 53 is done in-situ in a cluster tool as manufactured by Applied Materials. In FIG 12A, a silicon substrate 50 with a clean (no native SiO<sub>2</sub>) surface is the starting point. In FIG 12B, the lower layer 55 has been formed by oxidation/nitridation of the silicon substrate 50 to form a SiO<sub>x</sub>N<sub>y</sub> layer. In FIG 12C, a layer 56 of aluminum oxide has been formed by the inventive method, comprised of depositing aluminum oxide by chemical vapor deposition at temperatures greater than 500°C in the presence of an oxidant such as oxygen, ozone, N<sub>2</sub>O, H<sub>2</sub>O or

mixtures thereof. In FIG 12D, the upper layer 57 is formed by plasma nitridation of the aluminum oxide surface. In FIG 12E, polysilicon is deposited as the gate electrode 52. In FIGS 12F-12H, the gates are formed, extension implant done, spacers 58 formed, and source/drain implants performed to produce a fully formed devices. The subsequent steps of contact formation, etc., are not shown.

## EXAMPLE 6

Fabrication of a transistor with metal gates utilizing  
aluminum oxide deposited by the inventive method

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In this embodiment, the inventive method is used to fabricate a transistor using metal gates. As shown in FIG 1, a CMOS integrated circuit containing both n-type field effect transistors (NFETs) and p-type field effect transistors (PFETs) is formed on a single substrate 10. NFET device 11 is formed on a p-type conductivity region 13 of substrate 10 and contains a gate electrode 14 formed on a gate dielectric 15 and a pair of n-type source/drain regions 16 formed on laterally opposite sides of gate electrode 14. Similarly, PFET device 17 is formed on a n-type conductivity region 18 of substrate 10 and contains the gate electrode 19 formed on gate dielectric 15 and a pair of p-type conductivity source/drain regions 20 formed along opposite sidewalls of gate electrode 19. The NFET and PFET devices are separated by shallow trench isolation 21 and by spacers 22. In this embodiment, the gate electrode 14 or 19 is comprised of a bulk metal or alloy having the appropriate work function. Metals suitable for the gate electrode 14 of the NFET device 11 include, but are not limited to: Al, Ag, Bi, Cd, Fe, Ga, Hf, In, Mn, Nb, Y, and Zr or alloys thereof. At least one metal suitable for the NFET may also be alloyed with W, Mo, Cr, and Cu to form the gate electrode 14. Metals suitable for the gate electrode 19 of the PFET device 17 include, but are not limited to: Ni, Pt, Be, Ir, Te, Re and Rh. At least one metal suitable for the PFET may also be alloyed with W,

Mo, Cr, and Cu to form gate electrode 19. The subsequent steps of contact formation, etc., are not described. In this embodiment, the gate dielectric 15, which is selected from the group consisting of aluminum oxide or a multilayer structure wherein at least one of the layers is aluminum oxide, is deposited by the inventive method.

#### EXAMPLE 7

Process flow for fabrication of a transistor utilizing aluminum oxide deposited by the inventive method

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In this embodiment, the process flow used to fabricate a transistor using metal gates is described. FIG 22 shows a generic device structure including NFETs and PFETs. In this embodiment NFET and PFET are formed on a single p-type conductive substrate 60. NFET device is formed on a p-type conductivity region of substrate 60 and contains a gate electrode 62 formed on a gate dielectric 64 and a pair of n-type source/drain regions 65 formed on laterally opposite sides of gate electrode 62.

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Similarly, PFET device is formed on a n-type well 72 of substrate 60 isolated by shallow trench isolation 73 and contains the gate electrode 74 formed on gate dielectric 64 and a pair of p-type conductivity source/drain regions 76 formed along opposite sidewalls of gate electrode 74.

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FIGS 13 through 22 are partial cross sectional views showing one example of a possible fabrication sequence for a standard CMOS flow. In FIG 13, a silicon substrate 60 having shallow trench isolation (STI) 73 and an N-well 72 are formed in a portion of a p-type conductive substrate. In FIG 14, a gate dielectric 64 and a masking layer (for example  $\text{Si}_3\text{N}_4$ ) 77 have been formed on the substrate. The gate dielectric 64 may be deposited according to the inventive method. In FIG 15, an opening in the masking layer 77 where the NFET gate will go has been formed. In FIG 16, the NFET gate electrode 62 has



been formed. Materials suitable for the NFET gate electrode 62 include, but not limited to: polysilicon, W, Mo, Ti, Cr, Cu, Fe, Mn, Nb, V, Re, Pt, Ag, Bi, Cd, Fe, Ga, Hf, In, Mn, Y, Zr doped or undoped alloys, mixtures and multilayers thereof. The NFET gate electrode 62 may be deposited by the inventive method. In FIG 17, a chemical-mechanical polish (CMP) step has been done to planarize the surface. In FIGS 18 through 20, steps are shown which repeat those in FIGS 15-17 for the PFET device fabrication. In FIG 18, an opening in the masking layer 77 where the PFET gate will go has been formed. In FIG 19, the PFET gate electrode 74 has been formed. Materials suitable for the gate electrode 74 for PFET include, but not limited to: polysilicon, Ni, W, Mo, Ti, Cr, Te, Cu, Pd, Pt, Be, Au, Ir, Te, Rh, doped or undoped alloys, mixtures and multilayers thereof. The PFET gate electrode 74 may be deposited by the inventive method. In FIG 20, a chemical-mechanical polish (CMP) step has been done to planarize the surface. In FIG 21, extension implants are performed, one for the NFET, and one for the PFET, each through a blocking layer. In FIG 22, source/drain implants are performed, after a spacer 78 formation process, one for the NFET, and one for the PFET, each through a blocking layer to complete device fabrication. The subsequent steps of contact formation, etc. are not shown. In this embodiment, the gate dielectric 64, which is selected from the group consisting of aluminum oxide or a multilayer structure where at least one of the layers is aluminum oxide, is deposited by the inventive method.

## EXAMPLE 8

### Fabrication of a stack capacitor

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In this embodiment, an integrated circuit capacitor is fabricated incorporating aluminum oxide deposited by the inventive method. As shown in FIG 2, a typical capacitor is formed on a substrate 30, connected by a plug 31 to a transistor, with a barrier 32 and consists of a bottom electrode 33, a dielectric material 34 which may or may not be ferroelectric, and a top electrode 35. In this embodiment, the dielectric material, 34 aluminum oxide, is deposited by the inventive method.

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FIGS. 23 through 27 are partial cross sectional views showing one example of a possible fabrication sequence for a capacitor. In FIG 23, a substrate 30 having a trench is formed. Substrates include, but are not limited to: Si-containing semiconductor substrates, silicon on insulator substrates, Ge substrates, SiGe substrates, GaAs substrates, and other like substrates, dielectrics, metals, organic substrates, glasses, metal oxides, plastic polymeric substrates and mixtures, combinations and layers thereof. In FIG 24, a plug material 31 and an optional barrier 32 is formed. The plug material is composed of conventional conductive materials including, but not limited to: polysilicon, W, Mo, Ti, Cr, Cu, and may deposited utilizing the inventive method. The optional conductive barrier 32 is composed of conventional conductive materials including, but not limited to: TaN, TaSiN, TiAlN, TiSiN, TaSiN, TaWN, TiWN,

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TaSiN, TaAlN, NbN, ZrN, TaTiN, TiSiN, TiAlN, IrO<sub>2</sub>, SiC, TiPt, TiNPt, TiAlN-Pt, Ru, RuO<sub>2</sub>, RuPt, RuO<sub>2</sub>, WSi, Ti, TiSi, doped and undoped polysilicon, Al, Pd, Ir, IrO<sub>x</sub>, Os, OsO<sub>x</sub>, MoSi, TiSi, ReO<sub>2</sub>, mixtures or multilayers thereof and may be deposited utilizing the inventive method. In FIG 25, a bottom electrode 33 is formed. The bottom electrode is composed of conductive materials including, but not limited to: polysilicon, Ni, Pd, Pt, Cu, Ag, Au, Ru, Ir, Rh, IrO<sub>x</sub>, RuO<sub>x</sub>, TaN, TaSiN, Ta, SrRuO<sub>3</sub>, LaSrCoO<sub>3</sub>, doped or undoped alloys, mixtures, or multilayer thereof. In FIG 26, a dielectric material 34 is formed. The dielectric material is selected from the group consisting of aluminum oxide or a multilayer structure where at least one of the layers is aluminum oxide. The dielectric materials comprising the multilayer structure with aluminum oxide are selected from any insulating material including, but not limited to: SiO<sub>2</sub>, SiO<sub>x</sub>N<sub>y</sub>, Si<sub>3</sub>N<sub>4</sub>, metal oxides such as Ta<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, BaO, SrO, CaO, ZrO<sub>2</sub>, HfO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, alloys, mixtures or layers thereof, or multicomponent metal oxides such as perovskite type oxide having the formula ABO<sub>3</sub> wherein B is at least one acid oxide containing a metal selected from the group consisting of Al, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W and Cu, and A is at least one additional cation having a positive formal charge of from about 1 to about 3. Examples include, but are not limited to: barium strontium titanate, zirconate, or hafnate, lead titanate, yttrium aluminate, lanthanum aluminate, lead zirconium titanate, silicates such as hafnium silicate, zirconium silicate including rare earth doped silicates. In FIG 27, a top electrode 35 is formed. The top electrode is composed of conductive materials including, but not

limited to: polysilicon, Ni, Pd, Pt, Cu, Ag, Au, Ru, Ir, Rh, IrO<sub>x</sub>, RuO<sub>x</sub>, TaN, TaSiN, Ta, SrRuO<sub>3</sub>, LaSrCoO<sub>3</sub>, doped or undoped alloys, mixtures, or multilayer, thereof. The top and bottom electrode may or may not be similar. In this embodiment, the dielectric material 34, which is selected from group consisting of aluminum oxide or multilayer structure wherein at least one of the layers is aluminum oxide, is deposited by the inventive method.

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## EXAMPLE 9

### Fabrication of a trench capacitor

5 In this embodiment, an integrated circuit trench capacitor is fabricated incorporating at least one component deposited by the inventive method. One possible example for fabricating a trench capacitor on a substrate 30 is shown in FIG 28. A capacitor recess is  
10 formed in the substrate 30 which is connected to underlying circuitry via plug 31. The circuitry is covered with a dielectric insulating layer (isolation dielectric) 83. Substrates include, but are not limited to: Si-containing semiconductor substrates, silicon on  
15 insulator substrates, Ge substrates, SiGe substrates, GaAs substrates, and other like substrates, dielectrics, metals, organic substrates, glasses, metal oxides, plastic polymeric substrates and mixtures, combinations and layers thereof. The dielectric insulating layer  
20 (isolation dielectric) 83 is selected from any insulating material including, but not limited to:  $\text{SiO}_2$ ,  $\text{SiO}_x\text{N}_y$ ,  $\text{Si}_3\text{N}_4$ , phosphosilicate glass, or metal oxides such as aluminum oxide doped or undoped mixtures, or multilayers thereof. Over the plug and the capacitor recess is  
25 deposited in sequence, an optional conductive barrier layer 32, bottom electrode layer 33, dielectric layer 34, and a top electrode layer 35, and optional dielectric buffer layer 36. The plug material is composed of conventional conductive materials including, but not  
30 limited to: polysilicon, W, Mo, Ti, Cr, Cu, and may be deposited utilizing the inventive method. The optional conductive barrier 32 is composed of conventional

conductive materials including, but not limited to: TaN, TaSiN, TiAlN, TiSiN, TaSiN, TaWN, TiWN, TaSiN, TaAlN, NbN, ZrN, TaTiN, TiSiN, TiAlN, IrO<sub>2</sub>, SiC, TiPt, TiNPt, TiAlN-Pt, Ru, RuO<sub>2</sub>, RuPt, RuO<sub>2</sub>, WSi, Ti, TiSi, doped and undoped polysilicon, Al, Pd, Ir, IrO<sub>x</sub>, Os, OsO<sub>x</sub>, MoSi, TiSi, ReO<sub>2</sub>, mixtures or multilayers thereof and may be deposited utilizing the inventive method. The bottom electrode 33 is composed of conductive materials including, but not limited to: polysilicon, Ni, Pd, Pt, Cu, Ag, Au, Ru, Ir, Rh, IrO<sub>x</sub>, RuO<sub>x</sub>, TaN, TaSiN, Ta, SrRuO<sub>3</sub>, LaSrCoO<sub>3</sub>, doped or undoped alloys, mixtures, or multilayers thereof. The dielectric material, 34, is selected from the group consisting of aluminum oxide or a multilayer structure where at least one of the layers is aluminum oxide. The dielectric materials comprising the multilayer structure with aluminum oxide are selected from any insulating material including, but not limited to: SiO<sub>2</sub>, SiO<sub>x</sub>N<sub>y</sub>, Si<sub>3</sub>N<sub>4</sub>, metal oxides such as Ta<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, BaO, SrO, CaO, ZrO<sub>2</sub>, HfO<sub>2</sub>, aluminum oxide, La<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub> alloys, mixtures or layers thereof, or multicomponent metal oxides such as perovskite type oxide having the formula ABO<sub>3</sub> wherein B is at least one acid oxide containing a metal selected from the group consisting of Al, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W and Cu, and A is at least one additional cation having a positive formal charge of from about 1 to about 3. Examples include but are not limited to: barium strontium titanate, zirconate, or hafnate, lead titanate, yttrium aluminate, lanthanum aluminate, lead zirconium titanate, silicates such as hafnium silicate, zirconium silicate including rare earth doped silicates. The top electrode 35 is composed of conductive materials including, but not limited to:

polysilicon, Ni, Pd, Pt, Cu, Ag, Au, Ru, Ir, Rh, IrO<sub>x</sub>, RuO<sub>x</sub>, TaN, TaSiN, Ta, SrRuO<sub>3</sub>, LaSrCoO<sub>3</sub>, doped or undoped alloys, mixtures, or multilayer, thereof. The top and bottom electrode may or may not be similar. The optional dielectric barrier is composed of any insulating material including, but not limited to: SiO<sub>2</sub>, SiO<sub>x</sub>N<sub>y</sub>, Si<sub>3</sub>N<sub>4</sub>, TiON, AlN, SiN, TiN, metal oxides such as Ta<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, HfO<sub>2</sub>, aluminum oxide, La<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, alloys, mixtures or layers thereof, or multicomponent metal oxides. The sequentially deposited layers are planarized to yield a trench capacitor in the capacitor recess. An insulating passivation layer 37 and an inter-layer dielectric layer 38 are deposited to form a barrier structure over the trench capacitor in the capacitor recess. The insulating passivation layer 37 is composed of any insulating material including, but not limited to: SiO<sub>2</sub>, SiO<sub>x</sub>N<sub>y</sub>, Si<sub>3</sub>N<sub>4</sub>, TiON, AlN, SiN, TiN, metal oxides such as Ta<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, HfO<sub>2</sub>, aluminum oxide, La<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, alloys, mixtures or layers thereof, or multicomponent metal oxides. The inter-layer dielectric 38 is selected from any insulating material including, but not limited to: SiO<sub>2</sub>, SiO<sub>x</sub>N<sub>y</sub>, Si<sub>3</sub>N<sub>4</sub>, phosphosilicate glass, or metal oxides such as aluminum oxide doped or undoped mixtures, or multilayer, thereof. A via is formed in the barrier structure. A diffusion barrier layer 81 and a metallization layer 82 are deposited over the barrier structure and via. The diffusion barrier layer 81 includes, but not limited to: WN, TiN, or TaN. The metallization layer 82 is selected from any conductive material including, but not limited to: Al, W, Mo, Ti, Cr, or Cu doped or undoped alloys, mixtures, or layers thereof. In this embodiment, the dielectric material 34,

5 which is selected from the group consisting of aluminum oxide or a multilayer structure wherein at least one of the layers is aluminum oxide, is deposited by the inventive method; optionally aluminum oxide may be utilized as the dielectric including, but not limited to insulating passivation layer, inter-layer dielectric, diffusion barrier layer, isolation dielectric.



#### EXAMPLE 10

##### Fabrication of a Wiring Structure utilizing aluminum oxide

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In this embodiment, an integrated circuit wiring structure is fabricated incorporating at least one component deposited by the inventive method. As shown in FIG 3A, a typical wiring structure is formed by etching trenches 41 and vias 42 into a dielectric layer 43 selected from the group consisting of aluminum oxide or multilayer structures with aluminum oxide. The multilayer structures with aluminum oxide may consist of one or more layers selected from the group consisting of  $\text{SiO}_2$ ,  $\text{SiO}_x\text{N}_y$ ,  $\text{Si}_3\text{N}_4$ , phosphosilicate glass, or metal oxides doped or undoped mixtures, or multilayers thereof. The metallization layer may be patterned by a damascene or a dual damascene process or by lithography and etching. Below dielectric layer 43 is a metal thin film wire 44, selected from any conductive material including, but not limited to: Al, W, Mo, Ti, Cr, or Cu alloys, mixtures, or layers thereof, and a dielectric layer 45 selected from the group consisting of aluminum oxide or multilayer structures with aluminum oxide. The multilayer structures with aluminum oxide may consist of one or more layers selected from the group consisting  $\text{SiO}_2$ ,  $\text{SiO}_x\text{N}_y$ ,  $\text{Si}_3\text{N}_4$ , phosphosilicate glass, or metal oxides such as aluminum oxide doped or undoped mixtures, or multilayers thereof. In FIG 3B, the trench and via are filled with a barrier material 46, including, but not limited to: WN, TiN, or TaN and a wiring metal 47 selected from any conductive material including, but not limited to: Al, W,

Mo, Ti, Cr, or Cu doped or undoped alloys, mixtures, or layers thereof. In this embodiment, the dielectric layer 43 or 45, contains aluminum oxide deposited by the inventive method.

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While this invention has been particularly shown and described with respect to preferred embodiments thereof, it will be understood by those skilled in the art that the foregoing and other changes in forms and details may be made without departing from the spirit and scope of the present invention. It is therefore intended that the present invention not be limited to the exact forms and details described and illustrated, but fall within the scope of the appended claims.